New Developments in Catalysts for Producing a High-B.t.u. Gas via the Hot Gas Recycle Process

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INTRODUCTION

A high-B.t.u. gas can be produced from coal by gasifying the coal to make H_2+CO, and then reacting these gases, after purification, over a catalyst to make a gas consisting essentially of methane. (A satisfactory high-B.t.u. gas would have a minimum calorific value of 900 B.t.u. per cubic foot and a maximum carbon monoxide content of 0.1 percent.) A methanation process under development in the Federal Bureau of Mines at Bruceton, Pa., at the present time is the hot-gas-recycle process.

In the hot-gas-recycle system the exothermic heat of reaction (about 280 B.t.u. per cubic foot of methane produced) is absorbed by the sensible heating of large volumes of recycle gas circulating through the reactor in direct contact with the catalyst. Because of the large volumes of gas and the high cost of compression, it is necessary to have a low pressure drop through the catalyst bed. The development by the Bureau of an active, durable catalyst made of steel lathe turnings that pack with a high void volume and offer little resistance to flow made the hot gas recycle feasible.

This paper describes methanation in two stages using a steel lathe turning catalyst in the first reactor and nickel catalyst in the second to complete the conversion of synthesis gas. By this method the amount of nickel catalyst needed is considerably less than that usually required in methanation processes. Previous results have been reported for use of granular Raney nickel as catalyst in the second reactor.[1/] In this paper pilot plant results are shown comparing operation of the second reactor with granular catalysts and with nickel catalysts in the form of plates either of solid Raney nickel or nickel sprayed on steel or aluminum. These latter materials offer a negligible flow resistance and permit efficient use of a small amount of expensive nickel catalyst.

Table 1 shows the principal reactions occurring in the synthesis. Equations 1 and 2 are the synthesis reactions for the formation of hydrocarbons. Equation 3 is the water gas shift reaction. Equation 4 is an undesirable carbon deposition reaction, and 5 the carbide reaction. All these reactions are exothermic at synthesis temperature of 300° C.

TABLE 1. Reactions occurring in hot-gas-recycle process

1.	$3H_2 + CO$	$\rightleftharpoons$	$CH_4 + H_2O$
2.	$2nH_2 + nCO$	$\rightleftharpoons$	$(CH_2)_n + nH_2O$
3.	$H_2O + CO$	$\rightleftharpoons$	$CO_2 + H_2$
4.	$2CO$	$\rightleftharpoons$	$CO_2 + C$
5.	$2CO + 2Fe$	$\rightleftharpoons$	$CO_2 + Fe_2C$

EXPERIMENTAL PROCEDURE AND RESULTS

A flowsheet of the hot gas recycle process is shown in figure 1. Two reactors are used in series, the first, using steel lathe turnings, converts 70-90 percent of the synthesis gas, and the second, using nickel, converts essentially the remainder. The total feed gas passes down through the first reactor, then through a cyclone trap and is divided. Part flows to the second reactor; the remainder is recompressed to 425 p.s.i.g. and recycled to the reactor, 90 to 95 percent as hot recycle and the balance as cold recycle. As water is condensed and removed from the cold recycle, the amount of cold recycle is used to control the water vapor content of the total recycle gas. The synthesis gas then combines with the recycle gas and flows to the main reactor.

The tail gas flows to the second reactor which is operated at a lower recycle rate. In the absence of a hot-gas compressor, it was necessary to cool the whole recycle stream. The product stream is depressurized, metered, and analyzed.

Table 2 shows the results of typical tests operating with $3H_2+1CO$ feed gas using one or two reactors. The first column shows results achieved using only one reactor which contained steel turnings as catalyst. The turnings had been oxidized with steam and reduced with hydrogen to produce an active catalytic surface. The calorific value of the product gas was 720 B.t.u. per cubic foot. The carbon monoxide content was 2.1 percent. The methane content was 31.9 percent with significant quantities of ethane and propane. The feed-gas conversion was 83.4 percent. The second column of the table shows results obtained with both reactors operated in series. The second reactor contained Raney nickel of 4-20 mesh size. The heating value of the product gas increased to 986 B.t.u. per cubic foot, and the carbon monoxide content decreased to 0.1 percent. The methane content was 93.5 percent. In addition to methanating the carbon monoxide, most of the carbon dioxide reacted and the heavier hydrocarbons cracked and were hydrogenated to methane.

Because the Raney nickel catalyst used in the second reactor was in the form of granules, the pressure drop across the second reactor was higher than desired for hot-gas-recycle operation. Raney nickel is too brittle to be machined to lathe turnings, the physical form used for the catalyst in the first reactor. To overcome this difficulty, two types of nickel catalyst plates were devised. Plates were sawed from an ingot of Raney nickel and assembled in a parallel array to fit into the 3-inch diameter reactor as shown in figure 2. Plates were 5-3/4 inches high and 1/8 inch thick. A second type consisted of assemblies made of steel or aluminum plates sprayed with Raney nickel powder or nickel oxide powder using a oxy-hydrogen or oxy-acetylene torch. The powder of 100-300 mesh size was sprayed on 1/16-inch plates to a thickness of 0.040-0.060 inch on each side and edge. An average of 350 grams of Raney nickel or 250 grams of nickel oxide was on the surface of each assembly.

TABLE 2. Synthesis results using one or two reactors,[a] steel turnings in first reactor, granular Raney nickel in second

Reactors	1	2
Space velocity to first reactor, vol. of gas/vol. of catalyst/hour	850	850
Space velocity to second reactor	---	10,000
Exit gas analysis (vol.-percent-dry basis)		
H_2	48.6	2.8
CO	2.1	0.1
N_2	0.5	.8
CO_2	6.8	1.4
C_1	31.9	93.5
$C_2=$	0	0
C_2	5.4	0.9
$C_3=$	0.2	.1
C_3	2.9	.3
C_4+	1.6	.1
Heating value, B.t.u./cu. ft.	720	986
H_2+CO conversion, percent	83.4	99.3
Avg. temperature, °C. 1st reactor	320	319
Avg. temperature, °C. 2nd reactor	---	321

[a] $3H_2$+1CO feed to the first reactor.

The plate assemblies sprayed with Raney nickel were activated by digesting with a 3-percent NaOH solution to remove 20 percent of the aluminum. Those sprayed with nickel oxide were activated by reducing with hydrogen. The nickel oxide was a sinter material of the composition shown in table 3.

TABLE 3. Analysis of Raney nickel and nickel oxide[a]

Material	Raney nickel	Nickel oxide
Nickel	42-40	74.2
Aluminum	58-60	
Cobalt		1.04
Iron		1.94
Copper		0.73
Sulfur		.13

[a] Weight percent.

With the steel turnings being used as a catalyst in the first reactor, consecutive tests were made using solid Raney nickel plates, stainless steel plates sprayed with Raney nickel, and aluminum plates sprayed with nickel oxide sinter in the second reactor. At comparable conditions the pressure drop was reduced about 90 percent, from 17 inches with granular Raney nickel, to less than 2 inches of water per foot of catalyst height, with plates.

Table 4 shows other results of these tests. Except for the carbon monoxide content, a satisfactory high-B.t.u. gas was produced. No significant difference in catalyst activity or product composition was observed with these three catalysts in the second reactor. Since the nickel oxide sinter is as satisfactory as the Raney nickel as a catalyst for the second reactor, it would be preferred as it costs only one-third as much per weight of nickel.

TABLE 4. Results of tests using plate assemblies in second reactor[a/]

	First reactor	Second reactor		
Catalyst	steel turnings	Solid Raney plates	Raney nickel sprayed plates	Nickel oxide sprayed plates
Space velocity, vol./vol./hr.	700	6000	5800	5700
Avg. reactor temp., °C.	321	332	334	329
H_2+CO conversion, percent	73.8	97.3	98.0	97.5
Exit gas analysis, (vol.-percent-dry basis)				
H_2	56.7	9.0	7.5	9.0
CO	4.0	1.8	0.8	0.8
N_2	1.1	0.7	.8	.9
CO_2	8.7	2.4	2.1	2.6
CH_4	23.6	84.5	87.2	85.1
C_2=	0	0	0	0
C_2	3.5	1.0	1.0	1.1
C_3=	0.1	0.1	0.3	0
C_3-	1.7	.4	.3	.4
C_4=	0	0	0	0
C_4+	.6	.1	0	.1
Heating value, B.t.u./cu.ft.	566	925	943	927

a/ $3H_2$+1CO feed to the first reactor.

An advantage of the flame-spraying technique is evident with the nickel oxide. Nickel oxide granules disintegrated to powder on reduction with hydrogen at 400° C. Although the material was active catalytically, it had no mechanical strength. However, the nickel oxide sprayed on plates adhered firmly to the base metal after reduction. Thermal spraying may be applicable to other catalysts which are catalytically active but structurally weak.

Because the plates operated satisfactorily in the second reactor, a few tests were made using them in the first reactor. Table 5 shows the results of these tests. The solid plates of Raney nickel made a product gas with a heating value of 941 B.t.u. per cubic foot. The use of plates sprayed with Raney nickel resulted in gas with a heating value of 877 B.t.u. per cubic foot and the plates sprayed with nickel oxide, 856. In all cases the carbon monoxide content exceeded 0.1 percent. The plates sprayed with Raney nickel were operated at an average temperature of 255° C. When the temperature was raised to over 300° C. they became inactive.

TABLE 5. Results of tests using plate assemblies in first reactor[a/]

Catalyst	Solid Raney nickel plates	Raney nickel on stainless steel plates	NiO on aluminum or stainless steel plates
Space velocity, vol./vol./hr.	1250	1500	3000
Avg. reactor temperature, °C.	347	255	393
H_2+CO conversion, percent	99.0	93.1	95.4
Exit gas analysis (vol.-percent-dry basis)			
H_2	4.2	22.6	14.5
CO	0.3	4.3	1.7
N_2	1.3	0.4	1.2
CO_2	2.7	0.2	3.3
CH_4	91.4	63.5	79.3
C_2=	0	0	0
C_2	0.1	4.5	0
C_3=	0	0.1	0
C_3	0	1.7	0
C_4=	0	0.1	0
C_4+	0	0.7	0
Heating value, B.t.u./cu.ft.	941	877	856

a/ $3H_2$+1CO feed gas.

DISCUSSION

At an hourly space velocity of 6,000 and 330° C., sprayed nickel and solid Raney nickel plates produced a gas with the desired calorific value when used in the second stage of the hot gas recycle pilot plant. However, at this space velocity carbon monoxide values of 0.8 to 1.8 percent were too high. When used as a catalyst in the first reactor, at an hourly space velocity of 1,250 and 347° C., the solid Raney nickel plates produced a product gas of 941 B.t.u. per cubic foot and a carbon monoxide content of 0.3 percent, whereas the sprayed sections in the first reactor produced a gas that was unsatisfactory in both respects, calorific value and carbon monoxide content.

This difference in results between the solid Raney nickel plate assemblies and the plates sprayed with Raney nickel may be due to several factors: 1) The coating may have been too thin and the digestion procedure did not activate sufficient nickel; 2) the coating did not adhere to some of the plates, indicating either faulty sand blasting or spraying technique.

These nickel sections have advantages over steel lathe turnings. Higher conversions and higher heating value gas can be achieved in the first reactor; they can be operated at temperatures as high as 450° C. without significant carbon deposition; they are less susceptible to oxidation by steam, which means that the water vapor content of the recycle gas can be greater (less cold recycle gas). The pressure drop is less than with steel turnings, and because a greater temperature differential can be tolerated, a lower recycle flow is required. This decreases the cost of recompressing the recycle gas considerably. Other factors to be determined are the relative lives of the nickel and steel catalysts and their selective sensitivities to sulfur poisoning.

Other materials such as magnetite ore, fused iron oxide, and cobalt oxide have been sprayed on steel sections and tested in bench-scale units, but none were as active as the materials discussed.

CONCLUSIONS

While a good high-B.t.u. gas has been produced in one reactor using sprayed plates in the hot gas recycle process, it is not completely satisfactory according to the specifications. More tests are necessary to determine the optimum operating conditions to make a gas to meet this standard.

This technique of flame spraying catalysts on inert forms may have applications to other processes than hydrocarbon synthesis. Many metals and metal oxides can be sprayed. It is possible by proper technique to remove the base metal from the sprayed material and have a shape composed entirely of the catalyst.

REFERENCES

1. Bienstock, D., J. H. Field, A. J. Forney, and R. J. Demski, Pilot Plant Development of the Hot-Gas-Recycle Process for the Synthesis of High-B.t.u. Gas. BuMines Rept. of Investigations 5841, 1961, 27 pp.

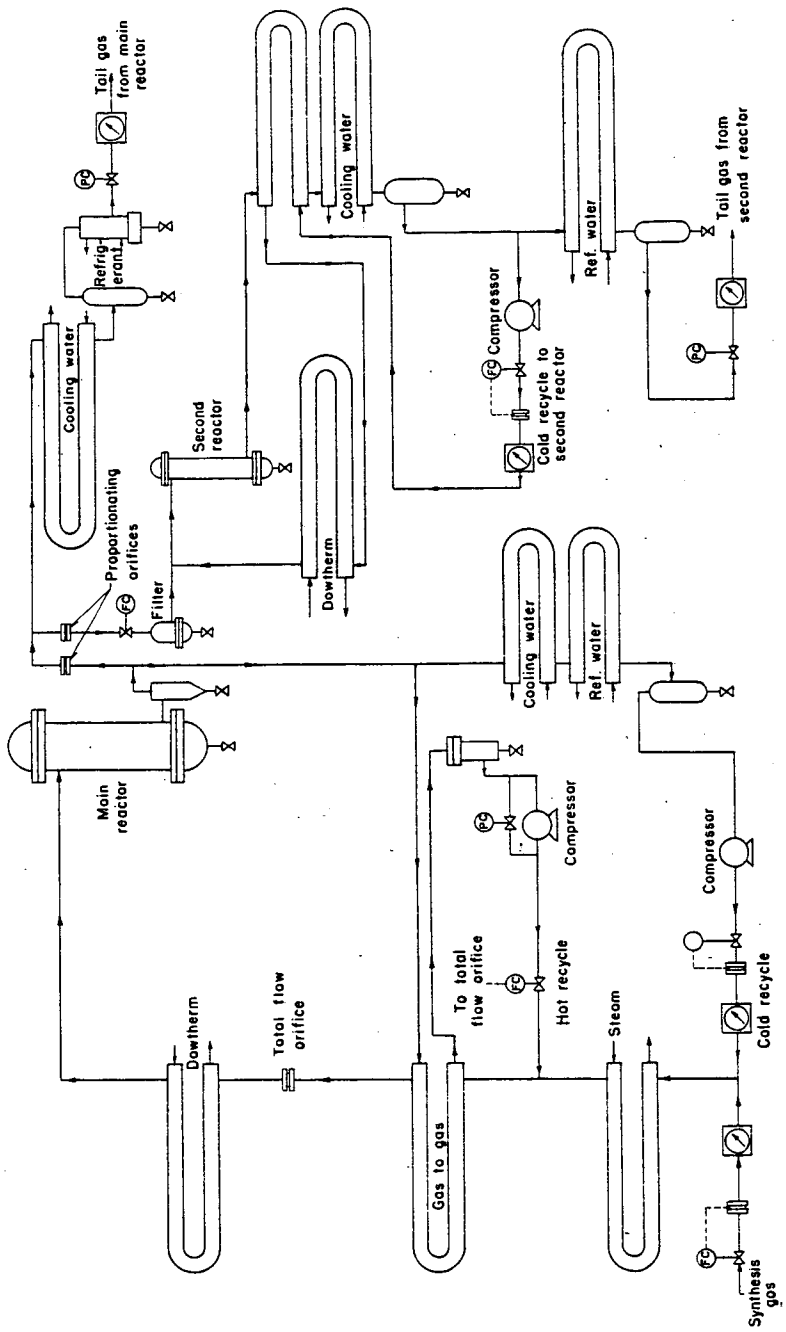

Figure 1. Flowsheet of hot gas recycle process for high-B.t.u. gas production.

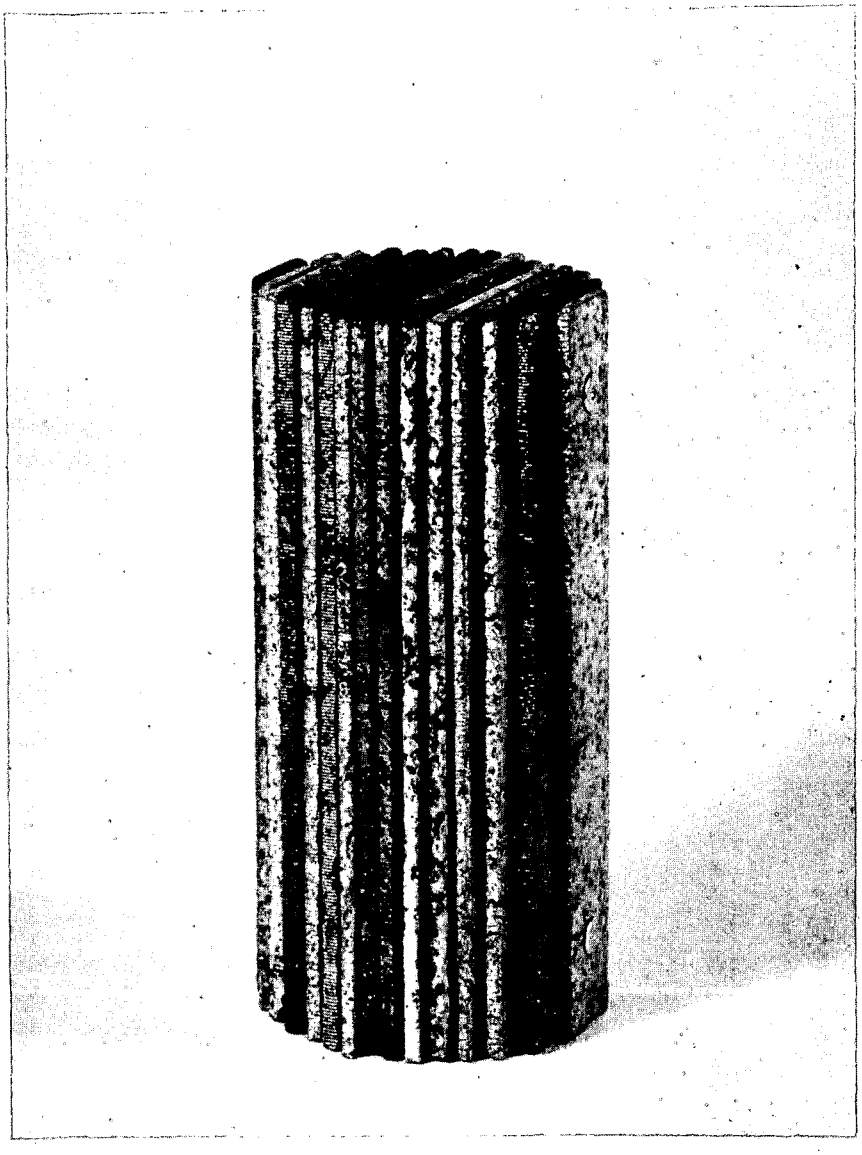

Figure 2. Parallel plate assembly of Raney nickel catalyst.